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TECHNICAL NOTE

ON THE ANALYSIS OF LINEAR  
PYROLYSIS EXPERIMENTS

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**TECHNICAL NOTE**

**ON THE ANALYSIS OF LINEAR  
PYROLYSIS EXPERIMENTS**

by  
**F. A. WILLIAMS**

**3-64-61-1**

**JUNE 1961**

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## FOREWORD

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## ABSTRACT

## Part One: A MODIFIED LINEAR PYROLYSIS EXPERIMENT

A linear pyrolysis experiment utilizing a heated porous plate is proposed and analyzed. Simple and chainlike surface gasification processes are defined and discussed. The conditions under which the surface process is a rate process or one of near equilibrium are determined in the general case and for chainlike processes. It is shown that pyrolysis measurements yield the forward gasification rate in the limit of a surface rate process and the equilibrium vapor pressure in the limit of surface equilibrium. The pyrolysis rate of potassium chloride is calculated.

## Part Two: REMARKS ON THE INTERPRETATION OF PYROLYSIS EXPERIMENTS ON AMMONIA SALTS

Previous interpretations by other investigators of linear pyrolysis rate measurements for  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{ClO}_4$  assumed that the surface process is an unopposed rate process. This report presents an alternative interpretation of pyrolysis experiments which may be valid even when the surface process is near equilibrium. Some features of a previously given analysis of a modified pyrolysis experiment (Part One) are employed to demonstrate that the difference between the plate temperature and the surface temperature of the solid may be large enough to affect seriously the activation energies which were calculated from the previous linear pyrolysis data.

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## NOMENCLATURE

$c_i$	$\sqrt{(R_3 T)/(2\pi W_i)}$ , average velocity of molecules of species $i$ in the $-x$ direction (cm/sec)
$c_{p,i}$	specific heat at constant pressure of gaseous species $i$ (cal/g°K)
$\bar{c}_p$	$(\partial h/\partial T)_{Y_i (i=1, \dots, N)} = \sum_{i=1}^N c_{p,i} Y_i$ , average specific heat of the gas (cal/g°K)
$D$	binary diffusion coefficient (cm <sup>2</sup> /sec)
$H$	$h + (v^2/2) (R_1/R_3)$ , total stagnation enthalpy per unit mass (cal/g)
$h$	$\sum_{i=1}^N h_i Y_i$ , total enthalpy per unit mass (cal/g)
$h_i$	total enthalpy per unit mass of gaseous species $i$ (cal/g)
$h_\pi$	total enthalpy per unit mass of the solid (cal/g)
$J$	$\sum_{i=1}^N Y_{i,s} h_i(T_s) - h_\pi(T_o) + (R_1/R_3) (v_s^2/2 - v_\pi^2/2)$ (cal/g); see Eq. (1.4)
$J'$	see p. 1-3, above Eq. (1.4)
$l$	thickness of the gas film (cm)
$M$	total number of chemical species leaving the solid surface
$m$	mass flow rate per unit area (g/cm <sup>2</sup> sec)
$N$	total number of gaseous chemical species
$P_i$	permeability of the porous plate to species $i$ (g/cm sec atm)
$p$	pressure (atm)

$p_{1,\infty}$	partial pressure of species $i$ at the downstream side of the porous plate (atm)
$p_\pi$	a constant in the momentum equation (atm); see Appendix A
$R_1$	universal gas constant, 1.986 (cal/mole°K)
$R_2$	universal gas constant, 82.06 (atm cm <sup>3</sup> /mole°K)
$R_3$	universal gas constant, $8.317 \times 10^7$ (g(cm/sec) <sup>2</sup> /mole°K)
$T$	temperature (°K)
$t$	thickness of the porous plate (cm)
$v$	mass-average velocity (cm/sec)
$W_i$	molecular weight of species $i$ (g/mole)
$w_i$	mass of molecules of type $i$ leaving a unit area of surface per second (g/cm <sup>2</sup> sec)
$x$	spacial coordinate (cm)
$Y$	$\sum_{i=1}^M Y_i$ , mass fraction of material leaving the solid surface
$Y_i$	mass fraction of gaseous species $i$
$\alpha$	accommodation coefficient (dimensionless)
$\beta$	$\sum_{i=1}^M \beta_i Y_{i,s} / Y_s$
$\beta_i$	$\alpha_i(\rho c_i)_s \int_0^l [dx/(\rho D)]$ , ratio of a characteristic diffusion time to a characteristic recondensation time
$\epsilon_i$	mass flux fraction of species $i$
$\eta$	$(4/3)\mu + \kappa$ , effective viscosity coefficient (g/cm sec)
$\kappa$	coefficient of bulk viscosity (g/cm sec)
$\lambda$	thermal conductivity of the gas (cal/cm sec°K)
$\mu$	ordinary (shear) viscosity coefficient (g/cm sec)

- $\xi$   $m \int_0^x [dx/(\rho D)]$  , dimensionless spacial coordinate  
 $\xi_p$   $m \int_0^{\ell} [dx/(\rho D)]$  , dimensionless mass flow rate  
 $\rho$  density (g/cm<sup>3</sup>)  
 $\sigma$   $\sum_{i=1}^N \sigma_i \epsilon_i$  , a dimensionless measure of the pressure at the porous plate  
 $\sigma_i$   $\left\{ (P_i p_p / t) \int_0^{\ell} [dx/(\rho D)] \right\}^{-1}$  , dimensionless permeability with respect to species  $i$   
 $\tau$  dimensionless surface temperature; see Eq. (1.15)  
 $\psi$   $\sum_{i=1}^N \sigma_i \psi_i / \sigma$  , dimensionless pressure on the downstream side of the porous plate  
 $\psi_i$   $(P_i p_{i,\infty} / t) \int_0^{\ell} [dx/(\rho D)]$  , dimensionless partial pressure of species  $i$  on the downstream side of the plate  
 $\omega$   $\sum_{i=1}^M \omega_i \beta_i / \beta$  , dimensionless forward surface gasification rate  
 $\omega_i$   $w_i / [\alpha_i (\rho c_i)_s]$  , dimensionless forward surface gasification rate of species  $i$

### Subscripts

- $e$  for surface equilibrium  
 $i$  a gaseous chemical species  
 $j$  a gaseous chemical species  
 $o$  at the upstream boundary of the solid ( $x = -\infty$ )

$p$  at the upstream edge of the porous hot plate  
 $r$  a reference condition at which the equilibrium vapor pressure is known  
 $s$  at the solid-gas interface  
 $\pi$  for the solid  
 $\infty$  at the downstream edge of the porous hot plate

Part One  
A MODIFIED LINEAR PYROLYSIS EXPERIMENT

1. INTRODUCTION

Schultz et. al. (Refs. 1-6) have reported many experiments on the linear regression rates of solids. These experiments have yielded pyrolysis rate data for pressures and temperatures approaching (but not yet equalling) those encountered in solid propellant rockets. These data are of considerable practical importance in predicting the deflagration rate of ammonium perchlorate (Ref. 7, pp. 612-618; Refs. 8-11) and, presumably, the burning rates of solid propellants (Ref. 12). Although the pressure is sufficiently high in these experiments so that the continuum equations of fluid mechanics may be applied to the gas adjacent to the solid, the geometry of the gas flow is so complicated that unquestionable interpretations of the significance of the measurements appear to be difficult to obtain. Consequently, it is of interest to investigate the possibility of modifying these experiments in order to yield data which can be interpreted more easily.

In Part One, an analysis is presented for a modified linear pyrolysis experiment which should not be difficult to perform. Conditions under which the surface process is a rate process or one of near equilibrium are determined for the modified experiment, and interpretations of the significance of the measurements are given for these two limiting cases. The pyrolysis rate of potassium chloride is computed as an example. The mathematical simplicity of the system described here provides a strong incentive to construct such an apparatus for measuring regression rates. The similarity of the present model to the previous pyrolysis experiments also enables us to draw some conclusions concerning the previous measurements.\*

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\*See Part Two.

## 2. MODIFIED EXPERIMENT

It is suggested that the hot plate used in previous pyrolysis experiments be replaced by a porous hot plate. If suitable shielding can be provided to prevent gas from escaping without passing through the porous plate, then the flow would be approximately one-dimensional, and the arrangement would appear as illustrated in Fig. 1-1.

Material gasifies from the solid surface at  $x = 0$  and flows through the porous plate at  $x = l$ . In analyzing this experiment, the gas phase and the interface conditions will be considered separately.

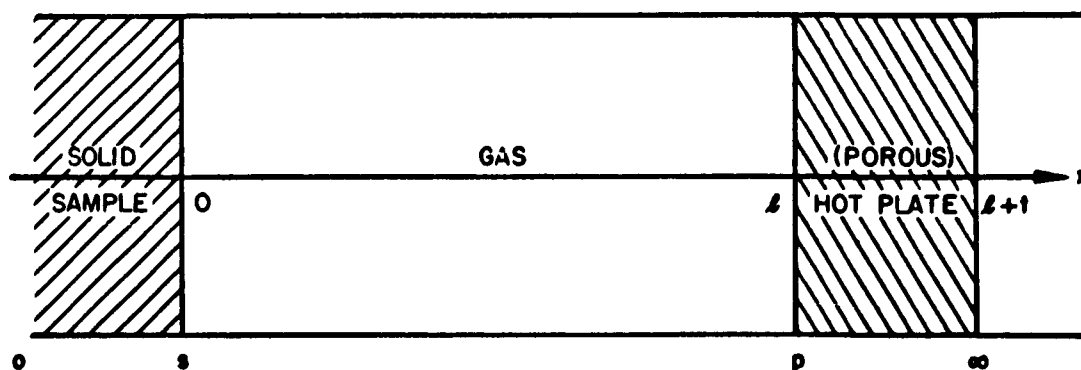


Fig. 1-1 Schematic Diagram of Modified Pyrolysis Experiment

## 3. ANALYSIS OF THE GASEOUS REGION

The one-dimensional, steady-state ideal gas conservation equations for total mass, the mass of species  $i$ , and energy are, respectively, \*

$$\rho v = m = \text{constant} \quad (1.1)$$

$$m \frac{dY_i}{dx} = \frac{d}{dx} \left( \rho D \frac{dY_i}{dx} \right), \quad i = 1, \dots, N \quad (1.2)$$

\*The basic equations are given in Ref. 13, pp. 234-241, for example. Symbols are defined in the Nomenclature. The momentum equation is considered in Appendix A.

and

$$m \frac{dH}{dx} = \frac{d}{dx} \left( \rho D \frac{dH}{dx} \right) \quad (1.3)$$

In Eq. (1.2), chemical reactions in the gas region have been neglected, and the binary diffusion coefficients of all pairs of chemical species have been assumed to be equal. Equation (1.3) relies upon the latter assumption, the approximation that the Lewis number is unity ( $\lambda = \rho D \bar{c}_p$ ), and the assumption that either the mass diffusivity equals the effective coefficient of viscosity ( $\eta = \rho D$ ) or the kinetic energy is negligible in comparison to the thermal plus chemical energy  $\left( \left[ \frac{R_1}{R_3} v^2/2 \right] \ll h \right)^*$ .

A boundary condition for Eq. (1.3) at  $x = 0$  is the requirement that enough heat must be conducted into the solid or generated at the solid surface by viscous dissipation to raise its temperature from  $T_0$  (at  $x = -\infty$ ) to  $T_s$  (at  $x = 0$ ) and cause gasification (including the accompanying enthalpy and kinetic energy changes) at  $T_s$ , i.e.,

$$\begin{aligned} (\lambda dT/dx)_s = & \sum_{i=1}^N \left[ m Y_{i,s} - (\rho D dY_i/dx)_s \right] h_i(T_s) - m h_\pi(T_0) \\ & + m \frac{R_1}{R_3} \left\{ \frac{1}{2} (v_s^2 - v_\pi^2) - \left[ (\eta/\rho) (dv/dx) \right]_s \right\} \equiv mJ' \end{aligned}$$

which may be written in the form

$$\begin{aligned} \left[ (\lambda/\bar{c}_p) (dH/dx) \right]_s = m \left\{ \sum_{i=1}^N Y_{i,s} h_i(T_s) - h_\pi(T_0) + (R_1/R_3) \right. \\ \left. \left[ \frac{1}{2} (v_s^2 - v_\pi^2) \right] \right\} \equiv mJ \quad (1.4) \end{aligned}$$

\*It is to be noted that  $\bar{c}_p$ ,  $\lambda$ , and  $\rho D$  may depend upon both  $T$  and  $Y_i$  in this formulation.

where the last term in the curly brackets is usually negligible. The boundary conditions for Eq. (1.2) at  $x = 0$  are

$$mY_{i,s} - (\rho D dY_i/dx)_s = m\epsilon_i, \quad i = 1, \dots, N \quad (1.5)$$

where  $\epsilon_i$  is the mass flux fraction of species  $i$  at the surface.\* Employing Eqs. (1.4) and (1.5) and denoting the boundary value at  $x = \ell$  as  $Y_i = Y_{i,p}$  and  $H = H_p$ , one finds the solutions to Eqs. (1.2) and (1.3) to be

$$Y_i = Y_{i,p} - (Y_{i,s} - \epsilon_i) (e^{\xi_p} - e^{\xi}), \quad i = 1, \dots, N \quad (1.6)$$

and

$$H = H_p - J(e^{\xi_p} - e^{\xi}) \quad (1.7)$$

where  $\xi \equiv m \int_0^x [dx/(\rho D)]$  and  $\xi_p \equiv m \int_0^x [dx/(\rho D)]$ .

#### 4. CONDITIONS AT THE POROUS PLATE

While the experimenter often has fairly direct control over the plate temperature  $T_p$ , the values of  $Y_{i,p}$  [which are needed along with  $T_p$  to determine  $H_p$  and  $Y_{i,p}$  in Eqs. (1.6) and (1.7)]\*\* will basically be determined by a permeability of the porous plate to species  $i$ ,  $P_i$ , and the partial pressure of species  $i$  on the downstream side of the plate,  $p_{i,\infty}$ . A reasonable phenomenological expression is obtained by

\*The values  $\epsilon_i$  are determined by the overall stoichiometry of the gasification process;  $\epsilon_i = 0$  for inert gaseous species (i.e., those not leaving the solid surface).

\*\*Strictly speaking, either  $v_p$  must also be measured or the momentum equation must also be solved (Appendix A) in order to determine completely the constants in Eq. (1.7). However, the kinetic energy will usually be negligibly small.

assuming that the mass flux is proportional to the pressure difference across the plate for each species, viz.,

$$mY_{i,p} - (\rho D dY_i/dx)_p = (P_i/t) \left\{ \left[ (Y_{i,p} p_p/w_i) / \left[ \sum_{j=1}^N (Y_{j,p}/w_j) \right] \right] - p_{i,\infty} \right\}, \quad i = 1, \dots, N \quad (1.8)$$

where  $p_p$  is the total pressure at  $x = \ell$ ,  $t$  is the thickness of the porous plate, and the first term inside the curly brackets is clearly the partial pressure of species  $i$  at  $x = \ell$ . In view of Eqs. (1.2) and (1.5), Eq. (1.8) may be written in the dimensionless form

$$(Y_{i,p}/w_i) / \left[ \sum_{j=1}^N (Y_{j,p}/w_j) \right] = \xi_p \sigma_i \epsilon_i + \sigma_i \psi_i, \quad i = 1, \dots, N \quad (1.9)$$

where  $\sigma_i \equiv \left\{ (P_i p_p/t) \int_0^\ell [dx/(\rho D)] \right\}^{-1}$  and  $\psi_i \equiv (P_i p_{i,\infty}/t) \int_0^\ell [dx/(\rho D)]$ .

Although only  $N-1$  of the  $Y_{i,p}$  are linearly independent, there are  $N$  independent relations in Eq. (1.9) since summing Eq. (1.9) over all species  $i$  gives the nontrivial equation

$$\sigma(\xi_p + \psi) = 1 \quad (1.10)$$

where

$$\sigma \equiv \sum_{i=1}^N \sigma_i \epsilon_i \quad \text{and} \quad \psi \equiv \sum_{i=1}^N \sigma_i \psi_i / \sigma = \sum_{i=1}^N p_{i,\infty} / \sum_{i=1}^N \left\{ [P_i/(\epsilon_i t)] \int_0^\ell [dx/(\rho D)] \right\}^{-1}.$$

This result is a consequence of the fact that Eq. (1.8) determines  $p_p$  in terms of

$\sum_{i=1}^N p_{i,\infty}$  and properties of the porous plate. If Eq. (1.10) is used to compute

the dimensionless plate pressure  $\sigma$ , then the remaining  $N-1$  independent relations in Eq. (1.9) will determine  $Y_{i,p}$ .

## 5. CONDITIONS AT THE SOLID SURFACE

A general surface condition, obtained by equating the mass flow rate of each species to the difference between the mass of that species leaving and entering the surface per second (Ref. 14; Ref. 15, pp. 60-71; Refs. 16 and 17) is

$$m\epsilon_i = w_i - \alpha_i Y_{i,s} (\rho c_i)_s, \quad i = 1, \dots, N \quad (1.11)$$

where  $w_i$  is the mass of molecules of type  $i$  leaving a unit area of surface per second,  $\alpha_i$  is a surface accommodation coefficient for species  $i$ ,  $c_i = \sqrt{(R_3 T)/(2\pi W_i)}$  is the average velocity of molecules of species  $i$  (of the ideal gas mixture) in the

$-x$  direction, and  $\rho = p / \left[ R_2 T \sum_{i=1}^N (Y_i / W_i) \right]$  according to the ideal gas law. Although the  $N$  independent relations in Eq. (1.11) should determine  $m$  and the  $N-1$  independent  $\epsilon_i$ , in most practical cases the overall surface stoichiometry is known more accurately than  $w_i$  or  $\alpha_i$ ; therefore, Eq. (1.11) would be used to determine  $m$  and to provide  $N-1$  relations between  $N-1$  of the  $w_i$  and  $N-1$  of the  $\alpha_i$ .<sup>\*</sup> Equation (1.11) may be written in the dimensionless form

$$\xi_p \epsilon_i = \beta_i (\omega_i - Y_{i,s}), \quad i = 1, \dots, N \quad (1.12)$$

<sup>\*</sup>It should be emphasized that  $w_i$  and  $\alpha_i$  may be functions of  $T_s$ ,  $p_s$  and all  $Y_{i,s}$  for complex surface processes.

where  $\beta_i \equiv \alpha_i(\rho c_i)_s \int_0^l [dx/(\rho D)]$  and  $\omega_i \equiv w_i/[\alpha_i(\rho c_i)_s]$ . From Eqs. (1.11)

or (1.12) it follows that, in general, the surface process with respect to species  $i$  will be a rate process similar to that encountered in vacuum vaporization or sublimation experiments (Refs. 17-19) if

$$Y_{i,s}/\omega_i = 1 - [(\xi_p \epsilon_i)/(\omega_i \beta_i)] \ll 1$$

while near equilibrium conditions prevail for species  $i$  at the surface if  $Y_{i,s}/\omega_i \sim 1$ , that is, if

$$(\xi_p \epsilon_i)/(\omega_i \beta_i) \ll 1.$$

## 6. GENERAL EQUATIONS FOR DETERMINATION OF PYROLYSIS RATE

If Eqs. (1.6) and (1.7) are evaluated at  $x = 0$ , and if Eq. (1.6) is solved for  $Y_{i,s}$  and Eq. (1.7) solved for  $\xi_p$ , then it is found that

$$Y_{i,s} = Y_{i,p} e^{-\xi_p} + \epsilon_i(1 - e^{-\xi_p}), \quad i = 1, \dots, N \quad (1.13)$$

and

$$\tau = e^{\xi_p} - 1 \quad (1.14)$$

where

$$\tau \equiv (H_p - H_s)/J \quad (1.15)$$

Utilizing Eq. (1.14), one may also write Eq. (1.13) in the form

$$Y_{i,p} - Y_{i,s} = (Y_{i,s} - \epsilon_i) \tau, \quad i = 1, \dots, N \quad (1.13a)$$

If Eq. (1.13a) is multiplied by  $h_i(T_s)$  and summed over all  $i$  and if use is made of Eq. (1.15) and the definitions of  $H$  and  $J$ , then by solving the resulting equation for

$$\left[ \sum_{i=1}^N (Y_{i,p} - Y_{i,s}) h_i(T_s) \right] / \left[ \sum_{i=1}^N (Y_{i,s} - \epsilon_i) h_i(T_s) \right] = \tau, \text{ it is found that}$$

$$\tau = \frac{\sum_{i=1}^N Y_{i,p} [h_i(T_p) - h_i(T_s)] + (R_1/R_3) \left( \frac{v_p^2}{2} - \frac{v_s^2}{2} \right)}{\sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_0) + (R_1/R_3) \left[ \frac{1}{2} (v^2 - v_\pi^2) \right]_s} \quad (1.15a)$$

From Eq. (1.15a) it is seen that  $\tau$  is physically a dimensionless measure of the unknown surface temperature  $T_s$ . Consider, for example, the special case in which kinetic energy and viscous dissipation are negligible and the specific heats of all gaseous species are constant and equal, whence Eq. (1.15a) becomes  $\tau = (T_p - T_s)/(J'/\bar{c}_p)$ .

Equations (1.9), (1.12), (1.13) and (1.14), plus the two equations obtained by summing  $Y$  over  $i$  at the surface and at the plate, basically constitute  $3N + 3$  independent equations in the  $3N + 3$  unknowns  $Y_{i,p}$ ,  $\sigma$ ,  $\xi_p$ ,  $\epsilon_i$ ,  $Y_{i,s}$ , and  $\tau$ . Appearing in these equations are the quantities  $W_i$ ,  $\sigma_i$ ,  $\psi_i$ ,  $\psi$ ,  $\beta_i$ , and  $\omega_i$ , which involve known parameters and known functions of the unknown variables. Hence it is presumably possible to solve this set of equations for the unknown variables and, in particular, to compute the dimensionless pyrolysis rate  $\xi_p$ .<sup>\*</sup> Essential features of the solution will best be illustrated by considering special simple cases.

<sup>\*</sup>In addition to the unknown pyrolysis rate,  $\xi_p$  actually also contains the length  $l$  which may be unknown in some experiments.<sup>p</sup> In such cases the momentum equation eventually determines  $l$  (Appendix A).

## 7. SIMPLE CHAINLIKE SURFACE PROCESSES

Many of the important characteristics of this problem may be deduced by examining the simplified set of equations henceforth referred to as the set (I) ,

$$\sigma = (\psi + \xi_p)^{-1} \quad (1.16)$$

$$Y_p = \sigma \xi_p \quad (1.17)$$

$$Y_s = 1 - (1 - Y_p)/(1 + \tau) \quad (1.18)$$

$$\xi_p = \ln(1 + \tau) \quad (1.19)$$

(I)

and

$$\xi_p = \beta(\omega - Y_s) \quad (1.20)$$

where  $\psi$  is a known constant,  $Y \equiv \sum_{i=1}^M Y_i$  , is the total mass fraction of all chemical species with  $\epsilon_i \neq 0$  (while  $\epsilon_i = 0$  for  $i = M + 1, \dots, N$ ) , and

$\beta \equiv \sum_{i=1}^M \beta_i Y_{i,s} / Y_s$  and  $\omega \equiv \sum_{i=1}^M \omega_i \beta_i / \beta = \left( \sum_{i=1}^M w_i \right) \int_0^l [dx / (\rho D)] / \beta$  are known

functions of  $\tau$  and  $\sigma$  alone. The general equations reduce to the set (I) for the simple chainlike surface processes discussed below.

If parallel competing surface reactions do not occur, a condition under which the surface process will be called chainlike, then the single concentration variable  $Y$  (which includes all of the chemical species leaving the solid surface) may be sufficient to characterize the composition of the gas for purposes of pyrolysis rate calculations.

Since  $\sum_{i=1}^M \epsilon_i = 1$  , Eq. (1.18) can be obtained by summing Eq. (1.13) from  $i = 1$

to  $i = M$  and utilizing Eq. (1.14) to eliminate  $\xi_p$ . Formally, Eq. (1.20) is obtained by summing Eq. (1.12) from  $i = 1$  to  $i = M$ . Equation (1.17) can be derived by summing Eq. (1.9) from  $i = 1$  to  $i = M$  when  $W_i = W_1 (i = 1, \dots, N)$ ,  $P_i = P_1 (i = 1, \dots, N)$ , and  $p_{i,\infty} = 0 (i = 1, \dots, M)$ ; if any of these conditions are violated, an expression for  $Y_p$  which is somewhat more complicated than Eq. (1.17) is obtained. The two remaining relations in set (I), Eqs. (1.16) and (1.19) are merely alternative forms of Eqs. (1.10) and (1.14), respectively.

Further restrictions are necessary in order to satisfy the additional requirement that  $\beta$  and  $\omega$  must depend only upon  $\tau$  and  $\sigma$ . The surface process may be called simple if  $w_i$  and  $\alpha_i$  depend upon  $T_s$  only, since gaseous concentrations  $(p_s, Y_{i,s})$  do not affect the surface rates in this case. Assuming  $W_i = W_1 (i = 1, \dots, N)$  and holding  $\int_0^L [dx/(\rho D)]$  constant, it follows from the definition of  $\beta_i$  and  $\omega_i$  that  $\alpha_i = \alpha_i(T_s)$  implies  $\beta_i = \beta_i(T_s, p_s)$  and that  $\alpha_i = \alpha_i(T_s)$  and  $w_i = w_i(T_s)$  together imply  $\omega_i = \omega_i(T_s, p_s)$ , whence the additional assumption  $\beta_i = \beta (i = 1, \dots, M)$  implies that  $\beta = \beta(T_s, p_s)$  and  $\omega = \omega(T_s, p_s)$  according to the definitions of  $\beta$  and  $\omega$ . If one neglects kinetic energy and viscous dissipation and assumes that the heat capacities of all species ( $i = 1, \dots, N$ ) equal  $\bar{c}_p$  between  $T_s$  and  $T_p$ , it follows from Eq. (1.15a) that (with  $T_p$  given)  $T_s = T_s(\tau)$ . The momentum equation (Appendix A) implies that  $p_s$  is determined by  $p_p$ , and, therefore, from the definition of  $\sigma$ ,  $p_s = p_s(\sigma)$ . Hence, under the conditions stated above,  $\beta = \beta(\tau, \sigma)$  and  $\omega = \omega(\tau, \sigma)$ . \*

\*Some consequences of the approximations  $\beta_i = \beta (i = 1, \dots, M)$ ,  $W_i = W_1 (i = 1, \dots, N)$ ,  $P_i = P_1 (i = 1, \dots, N)$ , and  $p_{i,\infty} = 0 (i = 1, \dots, M)$  are  $Y_{i,p} = \epsilon_i Y_p (i = 1, \dots, M)$  [see Eqs. (1.9) and (1.17)],  $Y_{i,s} = \epsilon_i Y_s (i = 1, \dots, M)$  [see Eqs. (1.13) and (1.18)], and  $\omega_i = \epsilon_i \omega (i = 1, \dots, M)$  [see Eqs. (1.12) and (1.20)]. While the present approximations are not unreasonable, in some cases it is possible to obtain  $\omega = \omega(\tau, \sigma)$  and  $\beta = \beta(\tau, \sigma)$  as well as the set (I) under much less stringent conditions.

# 8. THE FUNCTIONS $\beta(\sigma, \tau)$ and $\omega(\sigma, \tau)$ FOR SIMPLE CHAINLIKE SURFACE PROCESSES

For simple chainlike surface processes it is actually possible to obtain the  $T_s$  and  $p_s$  (i.e.,  $\tau$  and  $\sigma$ ) dependence of  $\omega$  explicitly. In general, in Eq. (1.11)  $m = m(T_s, Y_{i,s}, p_s)$ , whence, at constant  $p_s$ , Eq. (1.12) becomes

$$\xi_p(T_s, Y_{j,s}) \epsilon_i = \beta_i(T_s) [\omega_i(T_s) - Y_{i,s}] , i = 1, \dots, M \quad (1.21)$$

for simple surface processes. But, in surface equilibrium, which is defined by  $\xi_p = 0$ , it is a consequence of thermodynamics that, for chainlike surface processes,  $Y_{i,s} = Y_{i,s,e}(T_s)$ , where the subscript  $e$  identifies equilibrium conditions at the given constant  $p_s$ . Hence,

$$\epsilon_i \lim_{\substack{Y_{j,s} \rightarrow Y_{j,s,e} \\ T_s \text{ fixed}}} [\xi_p(T_s, Y_{j,s})] = 0 \quad i, j = 1, \dots, M \quad (1.22)$$

Substituting Eq. (1.21) into Eq. (1.22), one gets

$$\omega_i(T_s) = Y_{i,s,e}(T_s) , i = 1, \dots, M \quad (1.23)$$

Summing Eq. (1.23) from  $i = 1$  to  $i = M$ , one gets

$$\omega(T_s) = \sum_{i=1}^M Y_{i,s,e}(T_s) = Y_{s,e}(T_s) \quad (1.24)$$

when  $\beta_1 = \beta$ . Assuming that the gas is ideal, the density of the gas is negligible compared to that of the solid, and  $W_1 = W_1(i = 1, \dots, N)$ , the Clapeyron equation, becomes (Ref. 20, pp. 450-460)

$$d \left[ \ln(Y_{s,e} p_{s,e}) \right] = W_1 \left[ \sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_s) \right] dT_s / (R_1 T_s^2) \quad (1.25)$$

for this surface process. Integrating Eq. (1.25) at constant  $p_{s,e} = p_s (= p_{r,e})$  from a temperature  $T_r$ , at which the vapor pressure  $(Y_{r,e} p_{r,e})$  is known, to temperature  $T_s$ , one gets

$$Y_{s,e}(T_s) = Y_{r,e} \exp \left\{ - \int_{T_s}^{T_r} \frac{W_1 \left[ \sum_{i=1}^N \epsilon_i h_i(T) - h_\pi(T) \right]}{R_1 T^2} dT \right\} \quad (1.26)$$

Equations (1.24) and (1.26) give the  $T_s$  dependence of  $\omega$  explicitly. There is some evidence that  $\beta$  is not strongly dependent upon  $T_s$  at constant  $p_s$  for a few simple chainlike surface processes (Ref. 15, pp. 320-324). It is clear from the definition of  $\beta_i$  and  $\omega_i$  that  $\beta_i \sim p_s$  and  $\omega_i \sim 1/p_s$  for simple surface processes at constant  $T_s$ , whence also  $\beta \sim p_s$  and  $\omega \sim 1/p_s$ .

## 9. IMPLICATIONS OF THE SET (I) REGARDING THE GASIFICATION PROCESS

Using Eq. (1.16) for  $\sigma$  in Eq. (1.17), the result for  $Y_p$  in Eq. (1.18), this result for  $Y_s$  in Eq. (1.20), and Eq. (1.19) to eliminate  $\xi_p$  from the final expression, it is found that

$$\ln(1 + \tau) = \beta \left\{ \omega - 1 + (1 + \tau)^{-1} [1 + (1/\psi) \ln(1 + \tau)]^{-1} \right\} \quad (1.27)$$

which may be solved for  $\tau$ , after which Eqs. (1.16) through (1.19) give the remaining variables.

In the limiting case  $\tau \ll 1$ ,\* for all values of  $\psi$  except  $\psi \ll 1$ , Eq. (1.19) implies

$$\xi_p \approx \tau \quad (\ll 1) \quad (1.28)$$

Eqs. (1.16) and (1.17) imply

$$Y_p \approx \tau / \psi \quad (\ll 1) \quad (1.29)$$

and Eq. (1.27) becomes\*\*

$$\tau \approx \beta \omega / \left\{ 1 + \beta \left[ 1 + (1/\psi) \right] \right\} \quad (1.30)$$

Since the conditions for near equilibrium surface processes and unopposed surface rate processes given in Section 5 reduce to

$$\xi_p / (\omega \beta) \ll 1$$

and

$$1 - [\xi_p / (\omega \beta)] \ll 1$$

respectively, for chainlike surface processes, it is seen from Eqs. (1.28) and (1.30) that when  $\tau \ll 1$  the quantity

$$\xi_p / (\omega \beta) = \left\{ 1 + \beta \left[ 1 + (1/\psi) \right] \right\}^{-1} \quad (1.31)$$

\*This has been true in many of the pyrolysis experiments reported previously.

\*\*From Eqs. (1.18), (1.20) and (1.30), it is easily shown that  $[1 + (1/\beta) + (1/\psi)] \gg \omega > Y_s > Y_p$  when  $0 < \tau \ll 1$ .

determines whether equilibrium or rate conditions are valid at the surface. From Eq. (1.31) it is seen that (since  $\psi$  is not  $\ll 1$ ) near equilibrium conditions will prevail at the surface only if  $\beta \gg 1$ , while the surface process will be an unopposed rate process only if  $\beta \ll 1$ . From the definition of  $\beta$ , which represents the ratio of a characteristic diffusion time to a characteristic recondensation time, it can be seen that high pressure, large  $\ell$ , a large accommodation coefficient, and low diffusivities favor surface equilibrium.\*

In most pyrolysis experiments (Refs. 1-6),  $p = 1$  atm and  $300^\circ\text{K} \lesssim T_s \lesssim 900^\circ\text{K}$ . For reasonable  $\rho D$  and  $W_1$  ( $\rho D \approx 5 \times 10^{-4}$  g/cm sec,  $W_1 \approx 75$  g/mole),  $\beta/\alpha \ell = 5 \times 10^4 \text{ cm}^{-1}$  within a factor of 10. Since it is expected that one mean free path  $\sim 10^{-5}$  cm, it is therefore estimated that  $10^{-5} \text{ cm} \lesssim \ell \lesssim 10^{-2} \text{ cm}$ , and it follows that  $10^{-1} \alpha \lesssim \beta \lesssim 10^3 \alpha$ . Hence, for simple chainlike surface processes with  $\tau \ll 1$ , the surface process will probably be near equilibrium for  $\alpha = 1$  and a rate process for  $\alpha < 0.01$ .

## 10. INTERPRETATION OF PYROLYSIS RATE MEASUREMENTS

When the surface rate controls the pyrolysis rate (Section 9), then

$$\xi_p = \omega \beta \quad (1.32)$$

which implies  $m = \sum_{i=1}^M w_i$  according to the definition of  $\omega$  and  $\xi_p$ . Hence pyrolysis rate measurements yield directly the forward surface gasification kinetics. This has been the basis of interpretations of previous pyrolysis data (Refs. 1, 3, 5, 21-23).

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\*Since use has not been made here of the assumption that the surface process is simple, these results are valid for all chainlike gasification processes (with  $\tau \ll 1$  and  $\psi$  not  $\ll 1$ ).

When the surface process is near equilibrium, the left-hand side of Eq. (1.20) is much less than either term on the right; therefore the left-hand side of Eq. (1.27) is negligible. Utilizing Eq. (1.19) in Eq. (1.27), one gets

$$e^{-\xi_p} / [1 + (\xi_p/\psi)] = 1 - \omega \quad (1.33)$$

which shows that (knowing  $\psi$ ) a measurement of  $\xi_p$  determines  $\omega$ . When  $\tau \ll 1$  (and  $\psi$  not  $\ll 1$ ), Eq. (1.28) implies that Eq. (1.33) may be solved explicitly for  $\xi_p$  by expanding the left-hand side in powers of  $\xi_p$  and neglecting terms of higher than first order, viz.,

$$\xi_p \approx \omega / [1 + (1/\psi)] \quad (1.33a)$$

Equation (1.33a) is an expression which may also be derived from Eqs. (1.28) and (1.30), without using Eq. (1.33), by utilizing the previous result that  $\beta \gg 1$  near surface equilibrium when  $\tau \ll 1$ . Since  $\omega = Y_{s,e}$  at surface equilibrium [Eq. (1.20)], it follows from Eqs. (1.33) and (1.26) that for near equilibrium surface processes a pyrolysis rate measurement yields the equilibrium vapor pressure (provided  $l$ ,  $\rho D$ , and  $\psi$  are known), and that the dependence of the pyrolysis rate upon  $T_s$  determines the heat of gasification (even if  $l$ ,  $\rho D$ , and  $\psi$  are not known, so long as they remain constant).

## 11. PYROLYSIS RATE OF POTASSIUM CHLORIDE

As an example of the application of the preceding analysis we shall consider KCl, one of the few materials whose properties are sufficiently well known to permit an a priori calculation of the pyrolysis rate. Sublimation of KCl is a simple chainlike surface process (Ref. 22). In Fig. 1-2, the theoretical pyrolysis rate is plotted as a function of the plate temperature  $T_p$  for various values of  $l$  as computed from

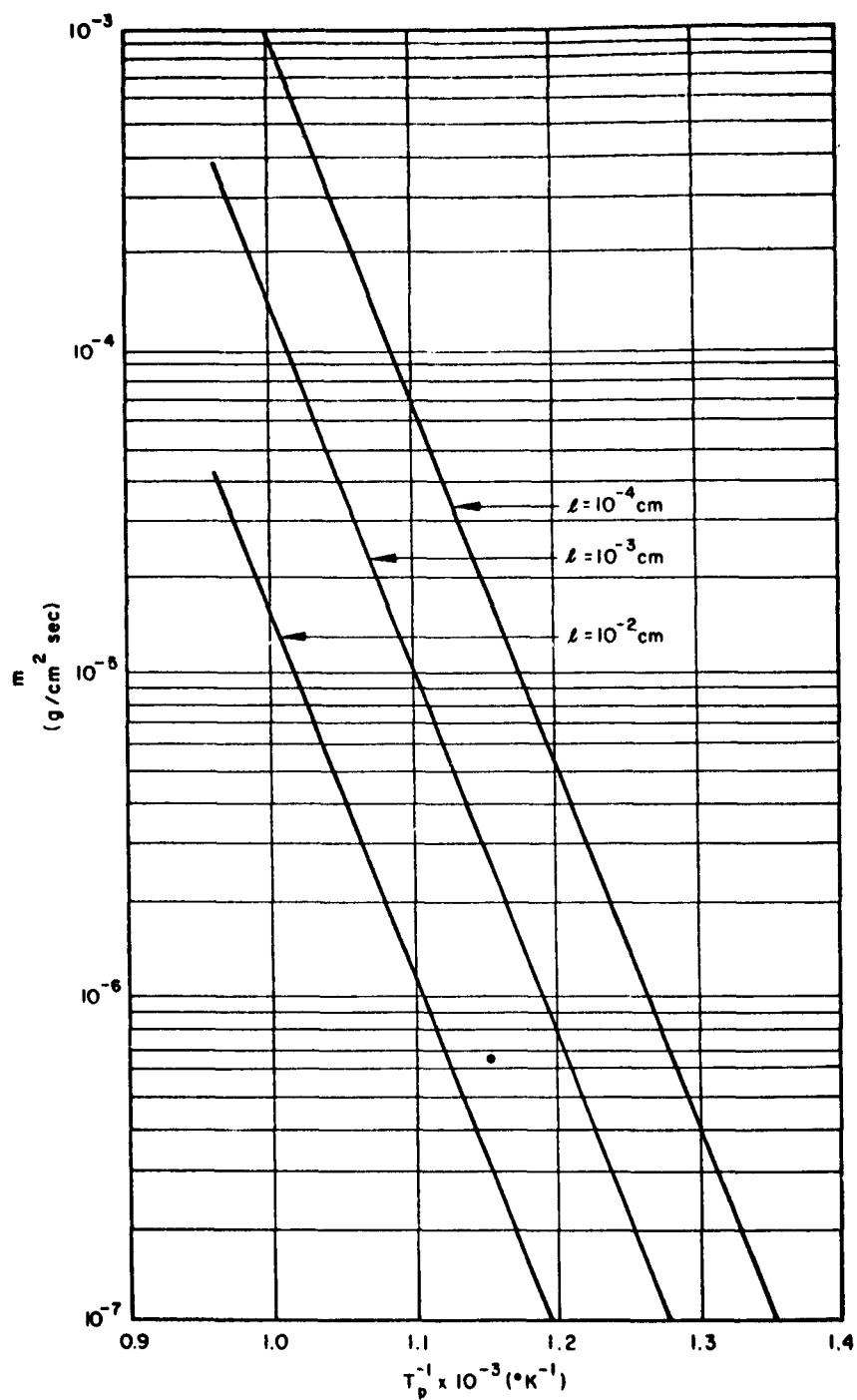


Fig. 1-2 The Linear Pyrolysis Rate of Potassium Chloride

the set (I) [using specifically Eqs. (1.19), (1.24), (1.26), and (1.27)] with  $1/\psi = 0$ ,  $T_0 = 300^\circ\text{K}$ , and  $p_s = 1\text{ atm}$ . Here (Refs. 22, 24, and 25)  $\bar{c}_p = 0.117\text{ cal/g}^\circ\text{K}$ ,

$$h_\pi(T_s) - h_\pi(T_0) = 0.166(T_s - T_0)\text{ cal/g}, \quad \sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_s) = 693\text{ cal/g},$$

$$\rho D = 5 \times 10^{-4}\text{ g/cm sec}, \quad \alpha = 0.63, \quad \text{and } Y_{s,e} = 6.4 \times 10^7 \exp(-26,070/T_s).$$

The computations were completed only for  $T_s$  less than the melting point ( $1049^\circ\text{K}$ ).

The results imply that surface equilibrium exists ( $\beta > 1$  provided  $\ell > 10^{-5}\text{ cm}$ )

and show that  $(Y_{s,e} - Y_s)/Y_{s,e} < 0.7$  (Fig. 1-3). Since it was always found that  $T_p - T_s < 5^\circ\text{K}$ , Eq. (1.33a) is actually valid here, and a pyrolysis rate measurement yields the equilibrium sublimation pressure.

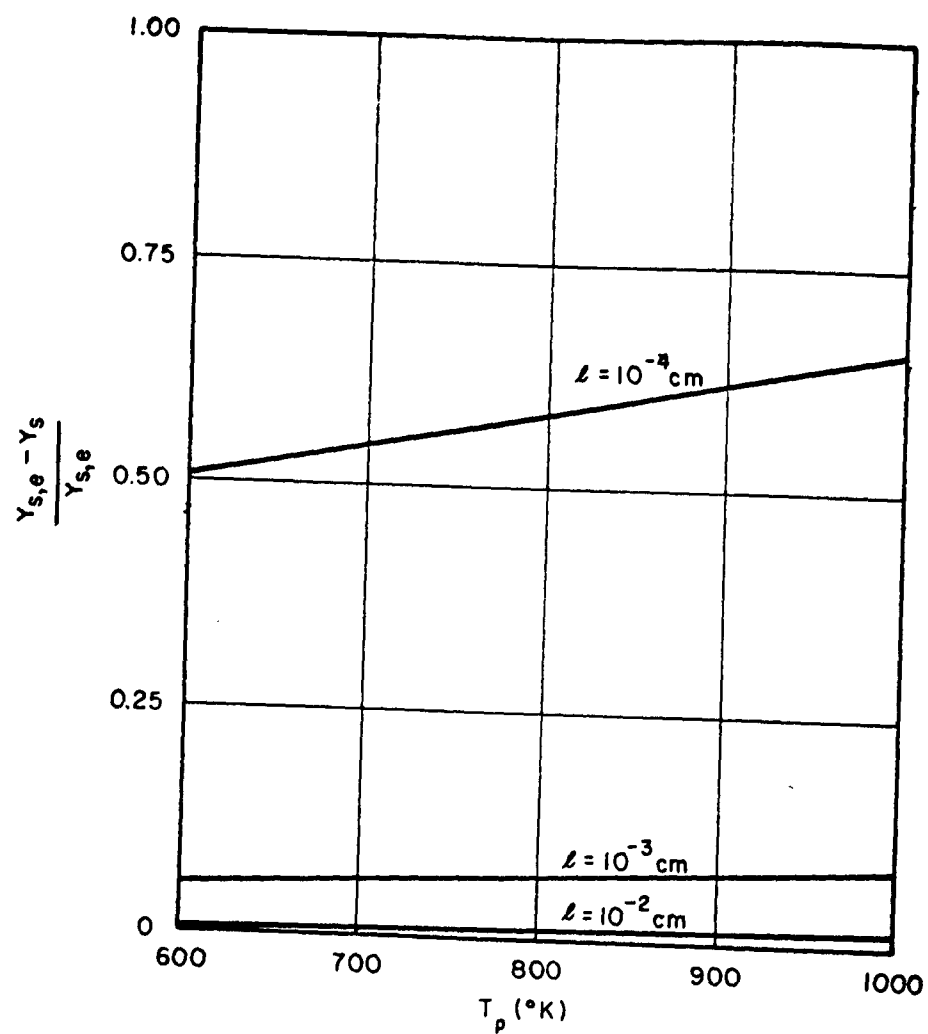


Fig. 1-3 The Departure of the Surface Mass Fraction of KCl From Its Equilibrium Value During Pyrolysis

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# Appendix A THE MOMENTUM EQUATION

In the gaseous region, the one-dimensional momentum equation is

$$m \frac{dv}{dx} + \left( \frac{R_3}{R_2} \right) \frac{dp}{dx} - \frac{d}{dx} \left( \eta \frac{dv}{dx} \right) = 0 \quad (\text{A. 1})$$

the first integral of which is

$$(R_3/R_2)p + mv - m dv/d\xi = (R_3/R_2)p_\pi = \text{constant} \quad (\text{A. 2})$$

when  $\eta = \rho D$ . The evaluation of the constant  $p_\pi$  depends upon the experimental arrangement. If the solid is supported in such a way that the spacing  $\ell$  is fixed,\* then  $p_\pi$  must be evaluated in the gas (e.g., at  $x = \ell$ ). If, however, only the gas layer supports the solid (i.e.,  $\ell$  is maintained by the pressure in the gas layer), then the momentum equation extends into the solid and  $p_\pi$  may be evaluated in the solid, where velocity gradients are negligibly small (i.e., viscous effects are negligible) and the dynamical pressure ( $mv_\pi$ ) is negligible (since  $\rho_\pi \sim 10^3 \rho_{\text{gas}}$  implies  $v_\pi \sim 10^{-3} v_{\text{gas}}$ ). Thus, in the latter case,  $p_\pi$  is the hydrostatic pressure in the solid, which equals the atmospheric pressure plus any additional pressure (applied force divided by cross-sectional area of sample) applied to the solid sample in order to increase "thermal contact" with the porous hot plate. While Eq. (A.2) and the ideal gas equation of state comprise the additional relations required to determine the distribution of all other properties (in particular,  $p$  and  $v$ ) in the gas, Eq. (A.2) cannot be integrated analytically.

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\*This appears to be the case in the previous pyrolysis experiments.

Considering the case in which viscous dissipation in the gas is negligible, Eq. (A.2) explicitly gives  $v$  in terms of  $p$ , viz.,

$$v = \frac{R_3}{R_2} (p_\pi - p)/m \quad (\text{A.3})$$

Utilizing Eq. (1.1) and the ideal gas law in Eq. (A-3), we find

$$p_\pi - p = m^2 \left( R_2^2 / R_3 \right) \left( \sum_{i=1}^N Y_i / W_i \right) T/p \quad (\text{A.4})$$

which determines  $p$  in terms of the variables  $Y_i$  and  $T$ . Equations (A.3) and (A.4) may, of course, be used to evaluate  $v_p$ ,  $p_p$ ,  $v_s$ , and  $p_s$  in terms of  $Y_{i,p}$ ,  $T_p$ ,  $Y_{i,s}$ ,  $T_s$ ,  $m$ , and  $p_\pi$ .

It may be noted that Eq. (1.10) and the relation obtained by evaluating Eq. (A.4) at  $x = \ell$  constitute two independent equations for the single unknown  $p_p$  (i.e.,  $\sigma$ ). By equating the values of  $p_p$  given by these two equations, an expression is obtained which may be solved for  $p_\pi$  if  $m$  is known or for  $m$  if  $p_\pi$  is known. In the former case  $m$  would be determined by the remaining governing equations (through  $\xi_p$ ) with  $\ell$  given, while in the latter case the pyrolysis rate is determined by the dynamic aspects of the problem and the remaining governing equations determine  $\ell$  (through  $\xi_p$ ) (Section 4). This is most easily illustrated in the case  $mv \ll \frac{R_3}{R_2} p$  (which is usually valid), whence Eq. (A.4) reduces to

$$p = p_s = p_p = p_\pi \quad (\text{A.5})$$

If  $P_i = P_1$  ( $i = 1, \dots, N$ ) and  $W_i = W_1$  ( $i = 1, \dots, N$ ), then summing Eq. (1.8) over all  $i$  yields

$$m = (P_1/t) (p_\pi - p_\infty) \quad (\text{A.6})$$

where use has been made of Eq. (A.5) and  $p_{\infty} \equiv \sum_{i=1}^N n_{i, \infty}$ . If  $l$  is fixed so that the other governing equations determine  $m$ , then Eq. (A.6) determines  $p_{\pi}$ ; if  $p_{\pi}$  is known, then Eq. (A.6) determines  $m$  directly.

Part Two  
REMARKS ON THE INTERPRETATION OF PYROLYSIS  
EXPERIMENTS ON AMMONIA SALTS

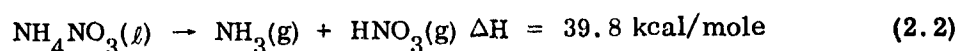
## 1. INTRODUCTION

Schultz and co-workers have reported linear pyrolysis rate measurements for  $\text{NH}_4\text{Cl}$  (Refs. 1 and 2),  $\text{NH}_4\text{NO}_3$  (Ref. 3), and  $\text{NH}_4\text{ClO}_4$  (Ref. 4), and have given consistent interpretations of their results based on absolute reaction rate theory (Refs. 1, 3, and 5). These interpretations rely upon the assumption that the surface process is an unopposed rate process (i.e., surface conditions are far from equilibrium). Since the pressure in the gas film between the pyrolyzing solid sample and the hot plate is probably sufficiently high for the continuum equations of fluid mechanics to be applicable in most of these experiments, it is conceivable that equilibrium surface conditions may be approached and that heat and mass transfer rates may be important in determining the measured pyrolysis rates. One purpose of these comments is to present an interpretation of the linear pyrolysis experiments which may be valid even in the limit in which fluid processes control the pyrolysis rate.

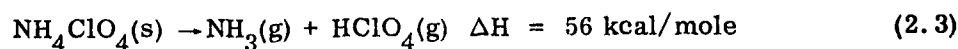
A detailed analysis (including heat and mass transfer) of a model of a modified pyrolysis experiment, in which the gases pass through a porous hot plate, has been given (Part One). Since this model has many features in common with the previously reported pyrolysis experiments, certain of the results in Part One may be used in interpreting pyrolysis rate measurements. In particular, the difference between the plate temperature and the surface temperature of the solid will be discussed. The symbols used are defined in the Nomenclature.

## 2. ALTERNATIVE INTERPRETATION OF PYROLYSIS EXPERIMENTS

It has previously been assumed that in pyrolysis of ammonia salts the overall surface process is one of dissociation (Refs. 2, 3 and 4), viz.,



and



This is an hypothesis which is supported by some evidence for dissociation in vacuum sublimation experiments (Refs. 1, 3, and 5-9). The  $\Delta H$  values listed here are obtained mainly from equilibrium vapor pressure measurements (Refs. 6, 7, 8 and 10), except in the case of  $\text{NH}_4\text{ClO}_4$  for which  $\Delta H$  must be calculated from the heats of formation since no vapor pressure measurements exist.

In the pressure and temperature range of the pyrolysis experiments, it may be true that either (1) the equilibrium composition is one with a negligible amount of dissociation, or (2) dissociation occurs in a gaseous process, the rate of which is small compared with the rate of escape of the gas from the film between the plate and the sample. In either of these cases, the overall surface process would be one of ordinary sublimation, not accompanied by dissociation. Since the surface accommodation coefficients  $\alpha$  for these processes are not known,\* it would still be impossible to predict, from an analysis similar to that given in Part One, whether the surface process is near equilibrium or a rate process. However, if the surface processes are simple chainlike

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\*Since the appropriate accommodation coefficients here are those for the undissociated vapor, previously reported accommodation coefficients (e.g., Ref. 6) are not applicable.

processes such as that encountered in KCl sublimation (Part One), then it may be expected that the temperature dependence of the pyrolysis rate would determine the heat of sublimation regardless of the importance of the fluid transfer processes (Part One). The pyrolysis results (Refs. 2, 3 and 4)\* are

$$m/p_{\pi} = 120 \exp [-13,500/(R_1 T_p)] \text{ cm/sec } (629^\circ \text{K} < T_p < 807^\circ \text{K}) \quad (2.4)$$

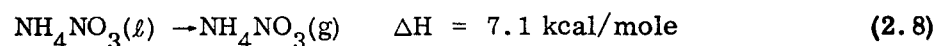
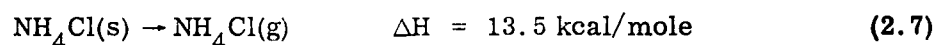
for  $\text{NH}_4\text{Cl}$ ,

$$m/p_{\pi} = 120 \exp [-7100/(R_1 T_p)] \text{ cm/sec } (453^\circ \text{K} < T_p < 573^\circ \text{K}) \quad (2.5)$$

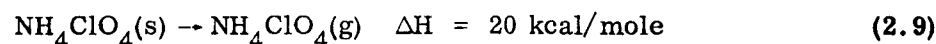
for  $\text{NH}_4\text{NO}_3$ , and

$$m/p_{\pi} = 4600 \exp [-20,000/(R_1 T_p)] \text{ cm/sec } (753^\circ \text{K} < T_p < 903^\circ \text{K}) \quad (2.6)$$

for  $\text{NH}_4\text{ClO}_4$ . These expressions would therefore imply that\*\*



and



respectively, in the temperature ranges indicated above. The  $\Delta H$  values given in Eqs. (2.7) through (2.9) would actually be valid for arbitrary types of surface processes if surface equilibrium prevails in the pyrolysis experiments, but must be restricted to simple chainlike processes if the surface conditions are far from equilibrium.

\*Undefined notation is the same as that used in Part One.

\*\*These  $\Delta H$  values rest on the assumption that  $T_p$  differs little from  $T_s$ ; in this connection see Section 3, Part Two, where improved  $\Delta H$  values are estimated.

We now briefly discuss each material separately, pointing out arguments for and against the processes given in Eqs. (2.7) through (2.9).

#### A. $\text{NH}_4\text{Cl}$

Since the pyrolysis data (Ref. 2) yield the same activation energy as the vacuum sublimation data (Ref. 6) and the low pressure equilibrium appears at present almost certainly to involve entirely dissociated  $\text{NH}_4\text{Cl}$  in the gas (Ref. 7), it follows that the new interpretation will be valid only if hypothesis (2) of the previous paragraph holds true. The large effect of  $\text{H}_2\text{O}$  in catalyzing the decomposition (Ref. 7) and the absence of  $\text{H}_2\text{O}$  from the dried  $\text{NH}_4\text{Cl}$  samples used in the pyrolysis experiments (Ref. 1) make it probable that the gas-phase dissociation is slow. The agreement between the data of Refs. 2 and 6 indicates that the surface sublimation is probably a rate process and  $\alpha < 0.01$  (Part One). The break in the experimental pyrolysis curve might result from an increase in the gas-phase dissociation rate.\*

#### B. $\text{NH}_4\text{NO}_3$

In pyrolysis,  $\text{NH}_4\text{NO}_3$  melts before gasification, and a change in the mechanism of gasification at the melting point causes the break in the experimental pyrolysis curve (Ref. 3). Since existing evidence indicates that in equilibrium the gas is completely dissociated (Ref. 8), hypothesis (2) seems more plausible than (1) for the temperature range of the pyrolysis experiments.

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\*Although it has been suggested that the break in the pyrolysis rate curve is caused by diffusion effects becoming rate controlling when the equilibrium dissociation pressure becomes less than atmospheric pressure (Ref. 2), this explanation is questionable on the grounds that the equilibrium dissociation pressure is always below atmospheric pressure for  $\text{NH}_4\text{NO}_3$  which exhibits no sharp decrease in  $\ln(m/p_\pi)$  with increasing  $1/T_p$ .

### C. $\text{NH}_4\text{ClO}_4$

In spite of the large amount of recent work on  $\text{NH}_4\text{ClO}_4$ ,\* there appears to be no conclusive experimental information to eliminate hypotheses (1) or (2). Evidence that some  $\text{NH}_4\text{ClO}_4$  condenses out of the gas, which was interpreted as favoring the dissociation process given in Eq. (2.3) (Ref. 9), is also consistent with Eq. (2.9). It has been pointed out (Ref. 11) that since the very strong acid  $\text{HClO}_4$  would have a much greater tendency to form hydrogen bonds than would  $\text{HNO}_3$  or  $\text{HCl}$ , it should favor the associated vapor  $\text{NH}_4\text{ClO}_4$ . Hence, the equilibrium associated vapor hypothesis (1) appears to have considerable theoretical justification. If the reaction in Eq. (2.9) is valid, then the pyrolysis experiments apparently provide the first determination of any thermodynamic property of undissociated  $\text{NH}_4\text{ClO}_4(\text{g})$ .

### 3. DIFFERENCE BETWEEN PLATE TEMPERATURE AND SURFACE TEMPERATURE

In the previous interpretations of the pyrolysis experiments it has been assumed that the plate and surface temperatures are approximately equal in order to compute activation energies for the surface process. It appears reasonable that in the pyrolysis experiments heat is transferred from the hot plate to the solid surface across the gas film by a conduction process which is essentially one-dimensional. If this is the case, then the difference between the plate temperature  $T_p$  and the surface temperature  $T_s$  can easily be estimated in terms of the observed pyrolysis rate. The appropriate one-dimensional heat conduction equation has, in fact, been solved in Part One [Eqs. (1.14) and (1.15a)], and the result may be written in the form

$$\bar{c}_p(T_p - T_s) / \left[ \sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_o) \right] = \exp \left\{ m \int_0^{\ell} [dx / (\rho D)] \right\} - 1 \quad (2.10)$$

\*See, for example, Eighth International Symposium on Combustion, Baltimore, Williams and Wilkins Co. (in press).

where use has been made of the fact that the pyrolysis rates are so small that kinetic energy and viscous dissipation are negligible. It should be emphasized that Eq. (2.10) relies upon none of the aspects of the model in Part One except the heat transfer equation.

Since  $\rho_\pi$  is  $1.527 \text{ g/cm}^3$  for  $\text{NH}_4\text{Cl}$ ,  $1.725 \text{ g/cm}^3$  for  $\text{NH}_4\text{NO}_3$ , and  $1.95 \text{ g/cm}^3$  for  $\text{NH}_4\text{ClO}_4$ , it follows from Eqs. (2.4) through (2.6) that  $m$  never exceeds  $0.35 \text{ g/cm}^2 \text{ sec}$ . Utilizing the reasonable values  $\rho D = 5 \times 10^{-4} \text{ g/cm sec}$  and  $l = 10^{-4} \text{ cm}$ , it is seen that  $m \int_0^l [dx/(\rho D)] \ll 1$ , whence the right-hand side of Eq. (2.10) may be expanded in powers of this quantity and powers higher than the first will be negligible. With the reasonable estimate  $\bar{c}_p = 0.2 \text{ cal/g}^\circ\text{K}$ , Eq. (2.10) then becomes

$$T_p - T_s = m \left[ \sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_o) \right]^\circ\text{K} \quad (2.11)$$

The quantity in the square brackets in Eq. (2.11) may be computed from the relations

$$\sum_{i=1}^N \epsilon_i h_i(T_s) - h_\pi(T_s) = \Delta H/W \quad (2.12)$$

and

$$h_\pi(T_s) - h_\pi(T_o) = c_{p,\pi,1}(T_t - T_o) + \Delta h_t + c_{p,\pi,2}(T_s - T_t) \quad (2.13)$$

where  $W$  is the molecular weight of the salt,  $T_t$  is a temperature at which a phase transition of the sample occurs,  $\Delta h_t$  is the heat of transition per unit mass, and  $c_{p,\pi,1}$  and  $c_{p,\pi,2}$  are the heat capacities of the sample below and above the transition temperature, respectively. For  $\text{NH}_4\text{Cl}$  (Refs. 6, 7, 10 and 12),  $W = 53.5 \text{ g/mole}$ ,

$T_t = 457.6^\circ \text{K}$  (a solid phase transition),  $\Delta h_t W = 1000 \text{ cal/mole}$ ,  $c_{p,\pi,1} W = 20.1 \text{ cal/mole } ^\circ\text{K}$ , and  $c_{p,\pi,2} W = 22.3 \text{ cal/mole } ^\circ\text{K}$ ; for  $\text{NH}_4\text{NO}_3$  (Refs. 8, 10, and 12),  $W = 80 \text{ g/mole}$ ,  $T_t = 442.8^\circ \text{K}$  (melting),  $\Delta h_t W = 1300 \text{ cal/mole}$ ,  $c_{p,\pi,1} W = 43.5 \text{ cal/mole } ^\circ\text{K}$ , and  $c_{p,\pi,2} W = 38.5 \text{ cal/mole } ^\circ\text{K}$ ; for  $\text{NH}_4\text{ClO}_4$  (Ref. 12),  $W = 117.5 \text{ g/mole}$ ,  $T_t = 513^\circ \text{K}$  (a solid phase transition), but since heat of transition data and heat capacity data appear to be absent, it will be assumed that  $\Delta h_t \approx 0$ ,  $c_{p,\pi,1} \approx c_{p,\pi,2} \approx 0.5 \text{ cal/g } ^\circ\text{K}$ ; and  $T_o = 300^\circ \text{K}$  in all cases. Utilizing this data and Eqs. (2.4) through (2.6) and (2.11) through (2.13), it is possible to solve for  $T_p - T_s$  as a function of  $T_p$  for all three salts, provided  $\Delta H$  values are known.

Using the values of  $\Delta H$  given in Eqs. (2.7) through (2.9), it is found that  $T_p - T_s$  varies from  $1^\circ \text{K}$  at  $T_p = 629^\circ \text{K}$  to  $14^\circ \text{K}$  at  $T_p = 807^\circ \text{K}$  for  $\text{NH}_4\text{Cl}$ , from  $9^\circ \text{K}$  at  $T_p = 453^\circ \text{K}$  to  $80^\circ \text{K}$  at  $T_p = 573^\circ \text{K}$  for  $\text{NH}_4\text{NO}_3$ , and from  $3^\circ \text{K}$  at  $T_p = 753^\circ \text{K}$  to  $40^\circ \text{K}$  at  $T_p = 903^\circ \text{K}$  for  $\text{NH}_4\text{ClO}_4$ . Thus, the assumption  $T_p \approx T_s$  is approximately valid for  $\text{NH}_4\text{Cl}$ , invalid for  $\text{NH}_4\text{NO}_3$ , and poor for  $\text{NH}_4\text{ClO}_4$ . It is interesting that the variation in  $T_p - T_s$  is such that the experimental checks employed indicate that the approximation  $T_p \approx T_s$  is valid; e.g.,  $T_p - T_s$  is relatively small at the melting point of  $\text{NH}_4\text{NO}_3$ , so that the break in the pyrolysis curve would occur at a value of  $T_p$  near the melting point.

If the larger  $\Delta H$  values in Eqs. (2.1) through (2.3) are used instead of those in Eqs. (2.7) through (2.9), then the calculated values of  $T_p - T_s$  are roughly doubled; it is clear that they must increase since the term  $m\Delta H/W$  enters on the right-hand side of Eq. (2.11). The estimate of  $\rho D \bar{c}_p$  used in this calculation should not be wrong by more than a factor of 5 and therefore cannot substantially modify our conclusion. Varying  $l$  does not alter the conclusion; if  $l$  is increased, the estimate of  $T_p - T_s$  increases [Eq. (2.10)], while when  $l$  is decreased, free molecule heat conduction sets in and the estimate of  $T_p - T_s$  changes very little. The result of  $T_p - T_s$  increasing substantially as  $T_p$  increases for  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{ClO}_4$  appears to be inescapable. A recent theoretical analysis by Cantrell (Ref. 13), in which a thin-film lubrication theory with heat transfer was used to account for the non-one-dimensional flow effects in pyrolysis experiments, also supports the contention that  $T_p - T_s$  is not small.

The main effect of the difference  $T_p - T_s$  is to modify the computed activation energy for the interpretation corresponding to Eqs. (2.1) through (2.3) and to modify the  $\Delta H$  values for the interpretation corresponding to Eqs. (2.7) through (2.9). For  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NH}_4\text{ClO}_4$ , respectively, the new activation energies are roughly 14 kcal/mole, 30 kcal/mole, and 30 kcal/mole, and the new heats of sublimation are very roughly 14 kcal/mole, 25 kcal/mole, 25 kcal/mole.

#### 4. FURTHER COMMENTS ON AMMONIUM PERCHLORATE

Use may be made of  $\text{NH}_4\text{ClO}_4$  deflagration experiments along with the pyrolysis experiments to provide an estimate of an upper bound for the accommodation coefficient, provided the surface process is a simple, chainlike, pure sublimation process [Eq. (2.9)] in both pyrolysis and deflagration. A result of the deflagration analysis of Johnson and Nachbar (Ref. 14) which is valid for this purpose is

$$Y_s = (T_f - T_s)/T^* \quad (2.14)$$

Certainly  $Y_s \leq Y_{s,e}$  for the deflagrating solid, and experimentally  $T_f - T_s \approx 116^\circ \text{K}$ , ( $T^* = 1415^\circ \text{K}$ ). This yields  $Y_{s,e} \geq 0.082$  at  $1100^\circ \text{K}$  and 100 atm. Since  $\xi_p \ll 1$  in the pyrolysis experiments, Eq. (1.20) implies

$$Y_{s,e} = (\xi_p/\beta) + Y_s \quad (2.15)$$

for simple chainlike surface processes. If we assume  $1/\psi = 0$  in the pyrolysis experiments, then Eqs. (1.16) through (1.19) imply  $Y_s = \xi_p$  when  $\xi_p \ll 1$ , whence we see

$$(\xi_p/\beta) + \xi_p = Y_{s,e} \quad (2.16)$$

If we utilize Eq. (1.26), with  $\Delta H = 20$  kcal/mole, to reduce the inequality  $Y_{s,e} \geq 0.082$  at  $1100^\circ \text{K}$  and 100 atm to another inequality on  $Y_{s,e}$  at  $900^\circ \text{K}$  and 1 atm (the conditions of the pyrolysis experiment), then Eq. (2.16) provides an inequality for  $[(\xi_p/\beta) + \xi_p]$ .

Since  $m$  is measured in the pyrolysis experiments, and  $f$  and  $\rho D$  are easily estimated (Section 3), the only unknown in the inequality is the accommodation coefficient  $\alpha$ . The result is roughly  $\alpha = 10^{-3}$ , which implies that the pyrolysis experiments are not near surface equilibrium. All of these conclusions rely strongly upon the pyrolysis model in Part One, the approximation of a simple chain-like surface sublimation process, and the experimental surface temperature estimates in deflagration.

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